



2002142

DATA EVALUATION RECORD

Freezer storage stability study of BAS 500 F, BF 500-3, BF 500-4, BF 500-5, BF 500-6 and BF 500-7

CAS NO: 175013-18-0

Pyraclostrobin (BAS 500 F)

171-4

MRID # 45367505

BASF Reg. #

Bolin, D. G., and M. G. Saha. 2001. Freezer storage stability study of BAS 500 F, BF 500-3, BF 500-4, BF 500-5, BF 500-6 and BF 500-7 in soil using LC/MS. BASF Study No. 52900. BASF Report No. A0015. Unpublished study performed and submitted by BASF Corporation, BASF Agro Research, Research Triangle Park, NC.

SECONDARY REVIEWER: Amer Al-Mudallal, Chemist
Environmental Risk Branch 1, EFED

SIGNATURE :

DATE : 11 / 5 / 02

CONCLUSIONS:

1- The study MRID # 45367505 is **unacceptable** and does not satisfy the guideline requirements for the following reasons:

- a. BAS 500 F and BF 500-3 did not degrade during frozen storage. However, the data were quite variable, and the variability may have masked some minor degradation.
- b. Average recoveries of BF 500-4 and BF 500-5 were 7-49 and 13-34% at 2 days-18 months posttreatment, respectively (Table I, pp. 23-24). The study author did not give an explanation for these low recoveries. Recoveries below 70% are typically due to inadequate analytical techniques.
- c. The test soil was not described or characterized. The physical and chemical characteristics, soil texture, and soil series were not reported. It was stated that the test soil was obtained from a terrestrial field dissipation study (Study No. 98016; MRID 45367502); however, that study involved Florida and California test sites with various soil types. Also, it was not stated whether the test soils used in the present study were moist or dry prior to fortification.

d. The limit of detection for the LC/MS analytical method was not reported. The limit of detection should be reported to allow the reviewer to evaluate the adequacy of the test method.

e. Chemical names of the degradates were not reported in the study.

f. Data for the 24-month samples were not included in the study report. The study authors stated that a final report will be submitted when those samples are analyzed (p. 15).

2- A new guideline study is needed to satisfy the freezer storage stability (171-4) requirements.

DATA EVALUATION RECORD

STUDY 4

PC No. 099100 Pyraclostrobin §171-4

CAS No.175013-18-0

DP Barcode D274092

FORMULATION-00-ACTIVE INGREDIENT

STUDY ID 45367505

Bolin, D. G., and M. G. Saha. 2001. Freezer storage stability study of BAS 500 F, BF 500-3, BF 500-4, BF 500-5, BF 500-6 and BF 500-7 in soil using LC/MS. BASF Study No. 52900. BASF Report No. A0015. Unpublished study performed and submitted by BASF Corporation, BASF Agro Research, Research Triangle Park, NC.

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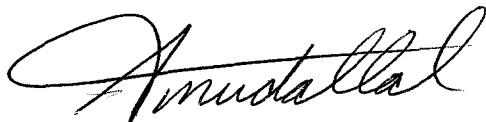
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ABSTRACT

Stability in Frozen Soil

The frozen storage stability of BAS 500 F (methyl-*N*-{2-[1-(4-chlorophenyl)-1*H*-pyrazol-3-ylloxymethyl]phenyl}(*N*-methoxy)carbamate), and degradates BF 500-3, BF 500-4, BF 500-5, BF 500-6, and BF 500-7 was studied in an unspecified soil. Soil samples were surface-treated with BF 500 and each degradate at a nominal concentration of 0.1 ppm, then stored frozen at $<-5^{\circ}\text{C}$ for up to 18 months. BAS 500F and BF 500-3 were relatively stable, BF 500-6 and BF 500-7 showed some degradation, and BF 500-4 and BF 500-5 degraded rapidly during the study.

Average recoveries of BAS 500 F were 104% of the applied at time 0, 98% at 3 months, varied from 92 to 97% at 4-9 months, were 102% at 12 months, 90% at 15 months, and 96% at 18 months. Average recoveries of BF 500-3 were 105% of the applied at time 0, varied from 90 to 99% at 2 days-12 months, were 82% at 15 months and 93% at 18 months. Average recoveries of BF 500-4 were 93% of the applied at time 0, decreased steadily from 49% at 2 days to 16% at 2 and 3 months, and were 7-12% at 9-18 months posttreatment. Average recoveries of BF 500-5 were 101% of the applied at time 0, decreased steadily from 34% at 2 days to 13% at 2 months, varied from 18-28% at 3-12 months, and were 14-15% at 15 and 18 months. Average recoveries of BF 500-6 were 102% of the applied at time 0, 86% at 2 months, 99% at 3 months, 84-87% at 4-12 months, 69% at 15 months, and 73% at 18 months. Average recoveries of BF 500-7 were 98% of the applied at time 0, 95-96% at 2 days-2 months, varied from 83 to 92% at 3-9 months, and were 75% at 15 months and 89% at 18 months. All data are reported as corrected for concurrent average procedural recovery

MATERIALS AND METHODS

Samples of soil (not described) obtained from a terrestrial field dissipation study were weighed individually (50 ± 0.1 g) and placed in plastic bags (p. 12). The samples were treated with BAS 500 F (methyl-*N*-{2-[1-(4-chlorophenyl)-1*H*-pyrazol-3-ylloxymethyl]phenyl}(*N*-methoxy)carbamate (IUPAC); Lot No. 00937-128, purity 99.8%; p. 10) and the degradates BF 500-3, BF 500-4, BF 500-5, BF 500-6 and BF 500-7, at a nominal application rate of 0.1 ppm (p. 12). The soil samples were directly treated with 1 mL of a 5 $\mu\text{g/mL}$ standard solution. The treated samples and several untreated control samples (each 50 ± 0.1 g) were stored frozen at $<-5^{\circ}\text{C}$ until analysis. Duplicate treated and three control samples were collected for analysis at 0 and 2 days, and 1, 2, 3, 4, 6, 9, 12, 15, and 18 months posttreatment. Two additional control samples treated with 0.1 ppm of standard solution containing BAS 500 F and the degradates served as procedural fortifications. Treated samples were also collected after 4, 7, 10 and 14 days of frozen storage for analysis of BAS 500-4 and BAS 500-5 (p. 6).

Soil samples treated with BAS 500 F and its degradates were extracted and analyzed using BASF Analytical Method Number D9812 (p. 13; Figure 1, p. 17). Soil samples

were extracted twice by shaking with acetonitrile then centrifuged (p. 13, Figure 1, p. 17). The acetonitrile extracts were combined, concentrated, triethylamine (100 μ L) was added, and the volume was adjusted. Aliquots were diluted with water containing 0.1% formic acid and 10 mM ammonium formate prior to analysis. Procedural fortification samples were further diluted with acetonitrile:water (70:30, v:v) containing 0.1% formic acid and 10 mM ammonium formate prior to analysis. The individual compounds were quantitated using LC-MS with APCI as the ionization source. Data were collected in positive mode with selected ion monitoring at m/z 388 (BAS 500 F), 358 (BF 500-3), 300 (BF 500-4), 195 (BF 500-5), 611 (BF 500-6), and 595 (BF 500-7).

Soil samples treated with BF 500-5 only were extracted and analyzed using BASF Analytical Method Number D9812/1 (p. 13; Figure 1, p. 18). Samples were extracted twice by shaking with acetonitrile and centrifuged. Unextracted soil residues were extracted with 0.1 N NaOH by shaking then were centrifuged. The resulting alkaline extract was acidified to \sim pH 2 using 2N HCl, and sodium chloride was added. The sample was extracted twice with ethyl acetate, and the resulting ethyl acetate extracts were combined and evaporated to dryness. The concentrated extracts were combined with the acetonitrile extracts, triethylamine was added, and the samples were concentrated and brought to volume with acetonitrile. Aliquots were diluted with water containing 0.1% formic acid and 10 mM ammonium formate. Procedural fortification samples were diluted with acetonitrile:water (70:30, v:v) containing 0.1% formic acid and 10 mM ammonium formate. The sample extracts were analyzed using LC-MS with APCI as the ionization source. Data were collected in positive mode with selected ion monitoring at m/z 195.

The limit of quantitation for BAS 500 F and metabolites in soil was 0.01 ppm for both the analytical methods (p. 14). The detection limit was not reported. Calibration curves of the reference substances were used for the quantitation of treated samples (Appendix A, Figures A.13-A.18, pp. 64-67).

RESULTS/DISCUSSION

The frozen storage stability of BAS 500 F (methyl-*N*-{2-[1-(4-chlorophenyl)-1*H*-pyrazol-3-yloxymethyl]phenyl}(*N*-methoxy)carbamate), and degradates BF 500-3, BF 500-4, BF 500-5, BF 500-6, and BF 500-7 was studied in an unspecified soil. Soil samples were surface-treated with BF 500 and each degradate at a nominal concentration of 0.1 ppm. The fortified soil samples were stored frozen at $<-5^{\circ}\text{C}$ for up to 18 months. BAS 500F and BF 500-3 were relatively stable, BF 500-6 and BF 500-7 showed some degradation, and BF 500-4 and BF 500-5 degraded rapidly during the study.

Average recoveries of BAS 500 F were 104% of the applied at time 0, 98% at 3 months, varied from 92 to 97% at 4-9 months, were 102% at 12 months, 90% at 15 months, and 96% at 18 months (Table I, p. 21). Average recoveries of BF 500-3 were 105% of the applied at time 0, varied from 90 to 99% at 2 days-12 months, were 82% at 15 months and 93% at 18 months (Table I, p. 22). Average recoveries of BF 500-4 were 93% of the

applied at time 0, decreased steadily from 49% at 2 days to 16% at 2 and 3 months, and were 7-12% at 9-18 months posttreatment (Table I, p. 23). Average recoveries of BF 500-5 were 101% of the applied at time 0, decreased steadily from 34% at 2 days to 13% at 2 months, varied from 18-28% at 3-12 months, and were 14-15% at 15 and 18 months (Table I, p. 24). Average recoveries of BF 500-6 were 102% of the applied at time 0, 86% at 2 months, 99% at 3 months, 84-87% at 4-12 months, 69% at 15 months, and 73% at 18 months (Table I, p. 25). Average recoveries of BF 500-7 were 98% of the applied at time 0, 95-96% at 2 days-2 months, varied from 83 to 92% at 3-9 months, and were 75% at 15 months and 89% at 18 months (Table I, p. 26). All data are reported as corrected for concurrent average procedural recovery.

DEFICIENCIES/DEVIATIONS

1. It appeared that BAS 500 F and BF 500-3 did not degrade during frozen storage. However, the data were quite variable, and the variability may have masked some minor degradation.
2. Average recoveries of BF 500-4 and BF 500-5 were 7-49 and 13-34% at 2 days-18 months posttreatment, respectively (Table I, pp. 23-24). The study author did not give an explanation for these low recoveries. Recoveries below 70% are typically due to inadequate analytical techniques.
3. The test soil was not described or characterized. The physical and chemical characteristics, soil texture, and soil series were not reported. It was stated that the test soil was obtained from a terrestrial field dissipation study (Study No. 98016; MRID 45367502); however, that study involved Florida and California test sites with various soil types. Also, it was not stated whether the test soils used in the present study were moist or dry prior to fortification.
4. The limit of detection for the LC/MS analytical method was not reported. The limit of detection should be reported to allow the reviewer to evaluate the adequacy of the test method.
5. Storage stability data for BAS 500 F, BF 500-3, BF 500-4, BF 500-5, BF 500-6 and BF 500-7 in various solutions are presented in Table XVI, p. 58.
6. The study authors stated that the level of fortification (0.1 ppm) was chosen to make recoveries less variable and to facilitate soil stability determinations for each analyte (p. 9).
7. Chemical names of the degradates were not reported in the study.
8. In the short-term study, soil samples fortified with only BF 500-5 were collected and analyzed after 2, 5, 7, 14, and 30 days of frozen storage. No time 0 samples were analyzed. The test soils were analyzed using two different methods to determine

extraction efficiency with the sodium hydroxide extraction procedure (BASF Analytical Method Number D98121/1) and without the sodium hydroxide extraction procedure (BASF Analytical Method Number D9812; p. 9). The results obtained using the two analytical methods were similar (Table 1, p. 25).

9. Data for the 24-month samples were not included in the study report. The study authors stated that a final report will be submitted when those samples are analyzed (p. 15).
10. Flow diagrams of the analytical methods are presented in Figures 1 and 2 (pp. 17-18).
11. Representative LC/MS chromatograms presented in Appendix A, Figures A.1-A.12 (pp. 60-64) indicated good separation of peaks.
12. Good Laboratory Practice Compliance and Quality Assurance Statements were provided with the study.

ATTACHMENT 1
Data Critical to the Study Interpretation

THE FOLLOWING ATTACHMENT IS NOT AVAILABLE ELECTRONICALLY
SEE THE FILE COPY